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14. ABSTRACT
The objectives of this project are to develop critical technlogies required for ZnO-based photonic device; high-quality ZnO film growth, p/n-doping processes, etching processes, and fabrication of ZnO light emitting devices. We have developed such critical technologies in this Phase I work. Prototype ZnO light emitting devices have been successfully fabricated and tested for a feasibility study to assess whether ZnO devices can satisfy the operational requirements as photonics devices to emit and detect UV light at room temperature. Based on these achievements, ZnO-based photonic devices can be used for defense applications. They wil be available in the market.

15. SUBJECT TERMS
ZnO-Based Light Emitting Devices, photonic devices, ZnO photonic devices, P-type ZnO, ZnO P-N Junctions, UV LEDs/LDs.

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Phase I Final Technical Report – 0001AD

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I. SUMMARY:

In accordance with our original program timetable for developing ZnO-based photonic devices, we have successfully completed goals associated with growth of p-type ZnO films, fabrication of ZnO p-n junctions, and fabrication and testing of prototype ZnO light emitting devices. These projects represent key milestones in our Phase I feasibility studies, and are important steps in preparation for the SBIR Phase II program. This report details specific achievements to date, including a description of activities for each stage of the original development schedule.

This report also provides information and goals for proposed SBIR Phase II program efforts..

II. MILESTONES:

The object of this Phase I SBIR program is to conduct a feasibility study of ZnO diodes for photonic applications. We have performed all tasks associated with each developmental stage as planned in this Phase I SBIR program. The milestones accomplished in developing ZnO diodes are as follows:

1) Substrate Surface Treatment for High-quality ZnO Film Growth - **Accomplished**
2) Ohmic Contacts to Arsenic (As)-doped p-type ZnO (ZnO:As) - **Accomplished**
3) ZnO p-n Junction Fabrication - **Accomplished**
4) ZnO Device Fabrication - **Accomplished**

III. TECHNICAL DEVELOPMENT PLAN:

Technical goals for each stage of the SBIR Phase I program that were established at the internal kick-off meeting were successfully achieved by each target date. The time-table for this program is given in Table 1 below. The detailed tasks to be completed for each stage of the SBIR Phase I program are as follows:

1) 1st Stage: June - July 2003 – **COMPLETED**
    - Find vendors to supply high-quality ZnO and SiC substrate wafers for high-quality ZnO film growth
    - Prepare for ZnO film growth–including surface treatment for n-type ZnO and n-type SiC substrates for best ZnO film growth
    - Synthesize p-type ZnO:As films on ZnO and SiC substrates
    - Make ohmic contacts to p-type ZnO:As films
    - Prepare ZnO multilayers for ZnO device growth
    - Write the first Progress Report
2) 2nd Stage: August – September 2003 - **COMPLETED**
    - Grow ZnO p-n junctions on ZnO and SiC substrates
    - Characterize ZnO p-n junctions and provide feedback for improving the quality of ZnO p-n junctions
    - Prepare masks for mesa structure, and fabricate ZnO diodes
    - Write the second Progress Report
3) 3rd Stage: September–November 2003 - **COMPLETED**
    - Fabricate ZnO diodes
    - Improve ZnO diode quality
    - Write the Draft Technical Report
4) 4th Stage: December 2003
    - Write the Final Report - **COMPLETED**
    - Prepare for the SBIR Phase II program - **COMPLETED**

Table 1. Work Schedule (June – December 2003)

work	June 11	July	Aug	Sept	Oct	Nov	Dec
Preparation	← - - - →						
Surface Treatment/ ZnO Film Growth	← - - -	- - - →			COMPLETED		
Metallization	← - - -	- - - →					
ZnO p-n Junction Growth			← - - -	- - - →			
ZnO diode Fabrication/Test				← - - -	- - -	- - - →	
Reports		Progress Report -1		Progress Report - 2		Draft Technical Report	Final Technical Report

IV. ACCOMPLISHMENTS:

We have successfully completed all of the planned work tasks for all Stages of the SBIR Phase I program for demonstrating feasibility for development of light emitting ZnO diodes. We have synthesized and characterized ZnO light emitting devices by using the results (namely, p-type ZnO film growth, ZnO p-n junctions and ohmic contacts) achieved in the 1st and 2nd Stages to fabricate and characterize ZnO light emitting diodes in the 3rd Stage. Results from these achievements demonstrate feasibility for producing ZnO light emitting devices.

A summary of achievements associated with the three Stages for the SBIR Phase I program is given below.

1st STAGE ACCOMPLISHMENTS

The 1st Stage work demonstrated that we were able to grow ZnO multilayers of p-type ZnO:As/n-type ZnO on n-type ZnO and n-type SiC substrates. Efforts included selection of wafer vendors, substrate surface treatment, p-type ZnO film growth, formation of ohmic metal contacts to p-type ZnO:As, and electrical characterization of p-n junctions. These achievements are summarized as follows:

Wafer Vendors

We found that high-quality ZnO and SiC wafers are supplied by several companies in the USA and in Japan–such as MTI Corp. (USA), Cermet Inc. (USA), Commercial Crystal Laboratories, Inc. (USA), Yamanaka Semiconductor Co. (Japan), Tokyo Denpa Co. (Japan), and Cree, Inc. (USA). In particular, production-grade SiC wafers (Cree) and hydrothermal-grown ZnO wafers (MTI) are very suitable for use in this ZnO diode development project. Recently, production-grade 2-in. dia., hydrothermal-grown ZnO wafers are being supplied by Tokyo Denpa Co.

Substrate Surface Treatment

Although single-crystal ZnO wafers are available in the commercial market, the surface quality of such ZnO wafers is not sufficiently high for high-quality ZnO film growth, due principally to the lack of an adequate polishing technology for ZnO. To overcome this problem, we developed a new process for cleaning ZnO substrates and for surface modification of the substrates that would promote high-quality ZnO film growth. A description of the method developed for substrate treatment is described in the following steps:

Solvent Cleaning of Substrates

The ZnO substrates are first cleaned by bathing with trichloroethane to help smooth the ZnO surface and help generate high-quality film growth. The surface treatment for ZnO substrates is performed for an interval 10 minutes at 70°C.

Note: Trichloroethane bathing is not necessary for SiC substrates.

Ultrasonic Cleaning of Substrates

After trichloroethane cleaning and prior to loading into the growth chamber, the substrates are cleaned ultrasonically first with pure acetone, then with methanol, and finally with deionized water at 70°C. After this process, the substrates are bathed twice with deionized pure water at room temperature to remove any residues remaining from the alcohol used for cleaning. The processing period for each step is about 10 minutes.

RF Oxygen Plasma Treatment

In the ultra-high vacuum chamber, before starting the film growth process, the substrate surfaces are treated for removal of contaminants such as carbon on the substrate surface as well as pre-oxidation by an rf-oxygen plasma source for 30 minutes at 800^0C. The rf discharge power to be used is 350 W, while the dynamical background pressure of oxygen in the chamber is 1×10^{-5} Torr.

The substrate temperature is then decreased until the designated growth temperature is attained, which is 550^0C for p-type ZnO:As film growth.

P-Type ZnO Film Growth—Hybrid Beam Deposition (HBD)

After rf-oxygen plasma treatment, p-type ZnO films were grown on O-ZnO and Si-SiC substrates in an oxygen pressure of 3×10^{-5} Torr, with substrate temperature at 550^0C. P-type ZnO films are obtainable by using As-atoms as an acceptor dopant. P-type ZnO:As films were synthesized by hybrid beam deposition (HBD). The HBD method used is very similar to a conventional MBE, but with two notable exceptions: (i.) a (Zn,O)-plasma is also employed, created by illuminating a polycrystal ZnO target with a pulsed ArF excimer laser, and (ii.) a high pressure of oxygen plasma, created by an rf-oxygen generator, is also used to promote ZnO film growth. An As-molecule beam was supplied from a Knudsen-type effusion cell, in addition to the (Zn,O)-plasma, to grow p-type ZnO films, with the laser repetition rate set at 20 Hz. A schematic of our HBD system is shown in Figure 1.

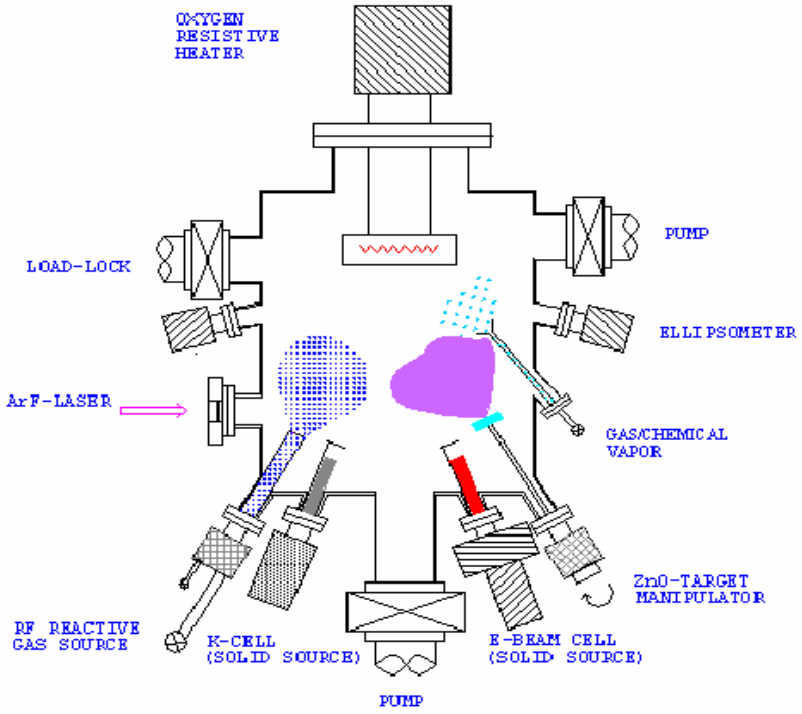


Figure 1. Schematic diagram of the HBD growth system. The characteristics of HBD allow use of different material sources for growth of high-quality ZnO and its alloys.

The desired value for As-element doping concentration was achieved by proper selection of the operating temperature of the As-effusion cell. Variation of the temperature over the range from 150 to 250^{0}C gave As-concentrations in the range from 10^{17} to 10^{20} cm^{-3} in the ZnO films. The film growth process was stopped by closing the As-cell shutter and by stopping laser beam illumination when the thickness of a doped ZnO film was about 1 μm. Without changing the substrate temperature, the deposited doped ZnO films would then be treated in an oxygen plasma of 5×10^{-5} Torr for 30 minutes. Following that treatment, the substrate temperature was then gradually decreased to room temperature at a rate of 10^{0}C/min. Finally, the power for the oxygen plasma was turned off, and the oxygen gas valve was closed to terminate pumping.

Using As as a dopant, we have successfully synthesized high-quality p-type ZnO films, having hole-carrier concentrations up to values in the low 10^{18} cm^{-3} region, with measured hole mobility values in the range from 1 to 50 cm^2/V-sec. These results are shown in a recent publication [Y.R. Ryu et al, Appl. Phys. Lett. 83, 87-89 (2003)]. The optical and electrical properties of p-type ZnO:As created by As-doping were presented and discussed.

For large-area film growth and to achieve high film growth rate, commercial HBD systems have been developed by VEECO under a contract with MOXtronics, Inc. In the commercial HBD, electron-beam evaporators will be employed *in lieu* of the ArF excimer laser for evaporation of ZnO to create the (Zn,O)-plasma. In addition, certain critical components used in the commercial HBD system will be designed to increase their resistance to oxidation.

Formation of Ohmic Metal Contacts to P-Type ZnO:As

For long-life operation of light emitting devices, efficient ohmic metal contacts should be available for ZnO. The method for making ohmic metal contacts to n-type ZnO is very well known; for example, indium (In) metal gives a good ohmic contact for n-type ZnO. However, there exists no report on how to make an ohmic contact to p-type ZnO. We succeeded in making a good ohmic contact to p-type ZnO:As by use of nickel (Ni) metal deposition followed by Au. These results were reported in our recent paper [Y.R. Ryu et al. Appl. Phys. Lett. 83, 4032-34 (2003)].

For development of ohmic metal contacts to p-type ZnO:As, different bilayer metal contacts were made by depositing either In, Ti, Ni, followed by deposition of a Au layer–all by electron beam evaporation. The current-voltage characteristics were then measured for each metal-to-ZnO:As contact. The As-doped ZnO films used for studying the metal-contact properties were grown on insulating, oxygen-face ZnO (O-ZnO) substrates with an As-concentration of 3 x 10^{18} cm^{-3}, similar in concentration level to p-type ZnO layers to be used in the fabrication of ZnO p-n junctions. The film thicknesses of the ZnO films used for this study were about 1 μm.

For all contacts, the thickness of the first layer of In, Ti, or Ni and the second Au layer were 30 nm and 100 nm, respectively. Their contact size was about 300×300 μm^2.

The current–voltage (I-V) characteristics of the metal contacts are shown in Fig. 2, 3, and 4.

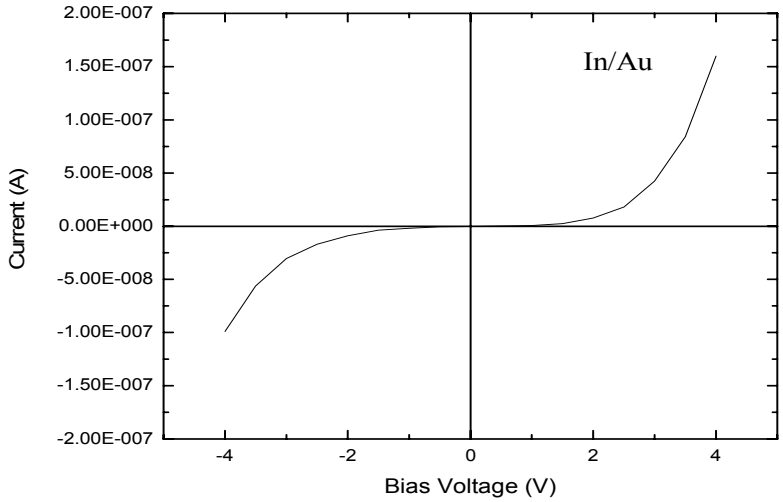


Figure 2. I – V characteristics of In/Au metal contacts on p-type ZnO:As films which show double (back-to-back) Schottky contact characteristics rather than ohmic contact characteristics.

For the same p-type ZnO films, Ni/Au contacts showed linear I-V characteristics, whereas In/Au and Ti/Au contacts showed the back-to-back Schottky barrier characteristics. Ni/Au contacts were ohmic to ZnO:As. These results demonstrate that the metallic composition of a contact to ZnO:As is critically important in order to achieve ohmic behavior. An annealing process at a high temperature in nitrogen or oxygen environment decreased contact resistance and increased adhesive force. For example, the I-V characteristics of Ni/Au metal contacts on p-type ZnO:As films were improved after annealing for 10 seconds at 600^0C in a nitrogen environment, as shown in Fig. 4.

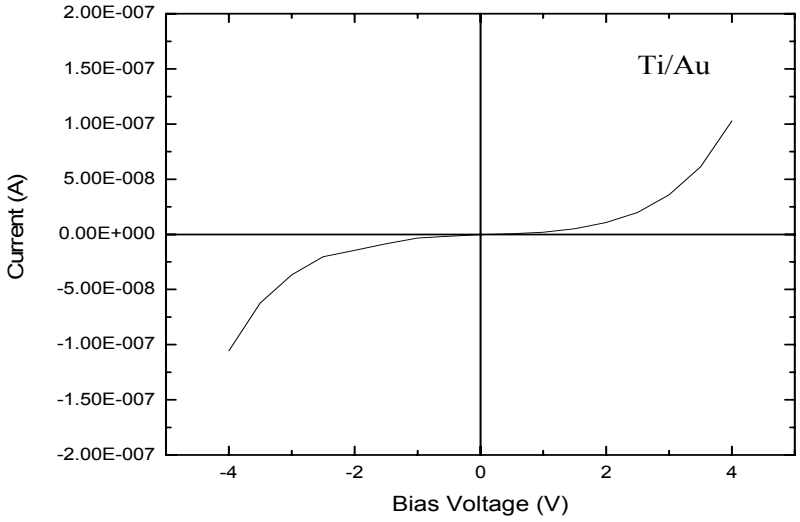


Figure 3. I – V characteristics of Ti/Au metal contacts on p-type ZnO:As films which show double (back-to-back) Schottky contact characteristics rather than ohmic contact characteristics.

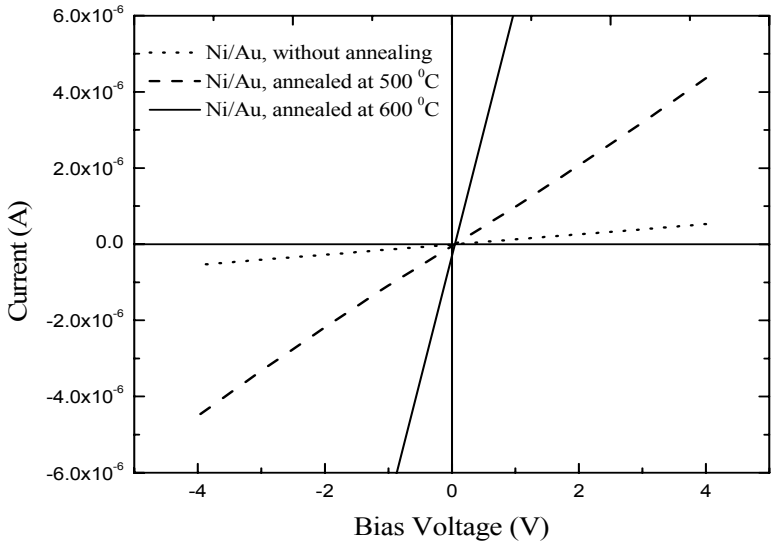


Figure 4. I – V characteristics of Ni/Au metal contacts on p-type ZnO:As films which show ohmic contact characteristics. Ohmic behavior has been improved with thermal annealing treatment.

2nd STAGE ACCOMPLISHMENTS

The 2st Stage work demonstrated that we were able to synthesize and characterize ZnO p-n junctions to help define the path to fabrication of ZnO light emitting diodes. These achievements are summarized as follows:

ZnO P-N Junction Growth

We grew p-ZnO layers on n-type ZnO layers deposited on n-type SiC (Si-faced 6H-SiC–Cree product-grade) substrates. SiC and ZnO substrates have a 3 x 10^{18} cm^{-3} electron concentration. Before ZnO layer growth, the substrates were treated by the surface cleaning process as reported above in the 1st Stage Accomplishments. ZnO p-n junctions were fabricated by HBD. For surface cleaning and oxidation, the SiC substrates were then treated with a rf plasma source of oxygen for 30 minutes at 800^0C before starting the growth process.

As the first step in the fabrication of a ZnO p-n junction, n-type ZnO films were grown on a surface–prepared SiC substrate using a (Zn,O)-plasma created by pulsed laser ablation of a ZnO target. The laser repetition rate was 20 Hz and the laser power per pulse was 100 mJ. The dynamic pressure of the oxygen plasma was fixed at 1 x 10^{-5} Torr during ZnO film growth. The substrate growth temperature was 650^0C, and the final film thickness for the undoped ZnO layer was about 0.2 μm. Hall-effect measurements showed such undoped ZnO films to be intrinsic n-type, with electron concentration values in the low 10^{17} cm^{-3} range, and mobility values near 100 $cm^2/V{\cdot}sec$.

After annealing at 550^0C for 10 minutes in a 5 mTorr oxygen plasma, an As-doped p-type ZnO layer was then grown on the n-type ZnO film by HBD. The growth temperature was 550^0C and the oxygen plasma pressure was 1 x 10^{-5} Torr. The As-concentration in the ZnO:As layer was 3 x 10^{18} cm^{-3}, which yielded a value of about 4 x 10^{17} cm^{-3} for the measured hole concentration [Y.R. Ryu et al., Appl. Phys. Lett. 83, 87 - 89 (2003)]. The p-type layer thickness was about 0.5 μm.

Characterization of ZnO P-N Layers

To measure I-V characteristics of ZnO p-n multilayer structures, ZnO films were first patterned for isolation with a mesa structure (500x800 μm^2) as shown in Fig. 5. The

I-V measurements were then performed with top-to-back contacts; specifically, as described in the section above on 1st Stage Accomplishments. Ni/Au (300×300 μm^2) metals were deposited on the top face (ZnO:As surface) of the mesa without an annealing process, and In/Au (300×300 μm^2) metals deposited on the back side of the SiC substrate, as schematically shown in Fig. 6.

The I-V curve for one such set of ZnO multilayer structures is shown in Fig. 6. The inset in Fig. 6 is the I-V curve of the same sample as grown, without mesa patterning. Such ZnO multilayer structures grown on n-type SiC were observed to have the I-V characteristics of a p-n junction diode with rather large turn-on voltages, in the range from 6 to 8 V. Although mesa patterning effectively decreases leakage current, high leakage current is still observed under reverse bias conditions, as shown in the semilog–plot inset in Fig. 6. The diode ideality factor (η) was derived using the expression, $I_F \sim \exp(qV_F/\eta kT)$, and obtaining the value of the slope in a $\ln(I_F)$ versus qV_F/kT plot, where V_F is the forward-biased voltage. The values of η obtained for these ZnO p-n junctions ranged from 3 to 5 at low voltages ($\leq$ 1 V), and in the range from 10 to 25 for higher voltages (> 1 V). The large deviation from the ideal ($\eta = 1$) means there exists a rather large leakage current through shunt resistance. Further studies will be required to fully understand the sources of such shunt resistance.

Either high contact resistance or ZnO layer resistance could create large turn-on voltages (6 – 8 V), as observed. As described earlier, an annealing process to reduce contact resistance is required in order to reduce the turn-on voltage such that its value is close to that for the ZnO energy bandgap. Work is in progress to improve the quality of ZnO p-n junctions through a combination of increasing the carrier density of ZnO layers, annealing, and film passivation. Improved quality would decrease observed values for turn-on voltages and leakage currents.

The electrical features of the In/Au-to-SiC contact, as well as the band offset between n-type SiC and n-type ZnO, should be considered before concluding that the observed I-V behavior originates within the ZnO p-n junction that is formed with p-type ZnO:As and n-type ZnO layers. For such an exploration, In/Au metals used for the top-to-back contacts were deposited on both sides of a pure n-type SiC substrate without ZnO layers, as well as on both sides of the sample composed of only n-type ZnO deposited on

n-type SiC, as schematically depicted in Fig. 7. The I-V curves in Fig. 7 clearly indicate that there exists a potential barrier, created by the presence of a Schottky barrier at the In/Au contact to n-type SiC. There exists also a band offset between the conduction bands of ZnO and SiC. The In/Au-contact to n-type ZnO does not affect the curve in Fig. 7(b) because it is a good ohmic contact to n-type ZnO. The magnitude for such a potential barrier can be roughly estimated. The Schottky barrier height (ϕ_b) can theoretically be estimated to be ≤ 0.2 eV by using the expression, $\phi_b = \phi_m$ (4.12 eV for indium) – χ (4 eV for SiC) [Waldrop, et al., Appl. Phys. Lett. 72, 4757 (1992)]. Schetzina measured the band offset between the conduction bands of ZnO and SiC, and found it small (≤ 0.3 eV) [Schetzina, US Patent 5,679,965]. Due to the presence of a Schottky contact and a band offset, there exists a small potential barrier (≤ 0.5 eV) in ZnO multilayer structures grown on n-type SiC. These results coupled with information from our I-V curves indicate that such a potential barrier negligibly affects the overall I-V characteristics for p-type ZnO/n-type ZnO multilayer structures on n-type SiC, as shown in Fig. 6. Thus, from Fig. 6 and Fig. 7, it can be determined that the rectification characteristics for the ZnO multilayer structures stem from properties associated with the p-type ZnO:As and n-type ZnO layers. These results were described elsewhere [Y.R. Ryu et al. Appl. Phys. Lett. 83, 4032-34 (2003)].

Based on these experimental breakthroughs, we successfully fabricated ZnO p-n junction diodes on n-type SiC substrates. These achievements allow fabrication of ZnO-based devices such as light emitting diodes and field-effect transistors. We are now fabricating and testing fabricated ZnO diodes for short-wavelength light emission.

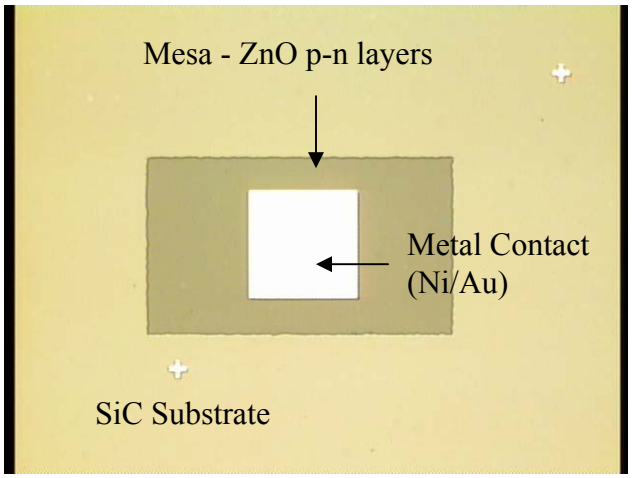


Figure 5. Microscopic image of a mesa-patterned ZnO p-n junction.

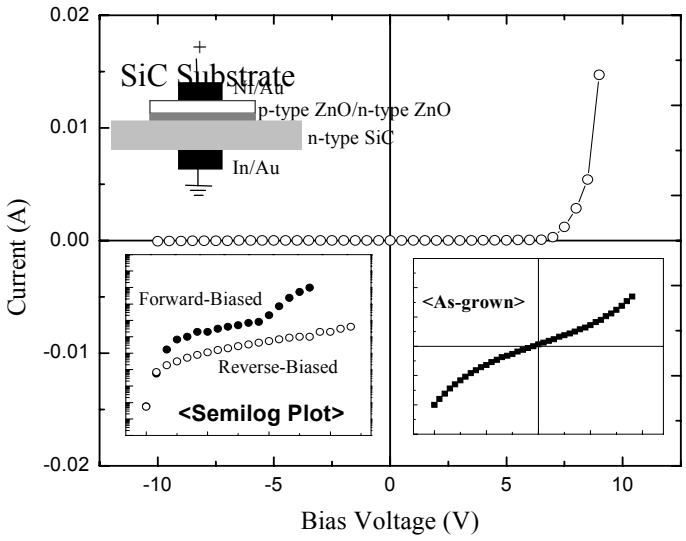


Figure 6. I–V characteristics of a ZnO p-n junction displaying rectifying behavior. Proceeding from the upper left quadrant in a counterclockwise direction, the respective insets are as follows: schematic for a ZnO p-n junction used for measuring the I–V characteristics, the I– V plot on a semilog scale, and the I–V curve from the as-grown sample without mesa patterning.

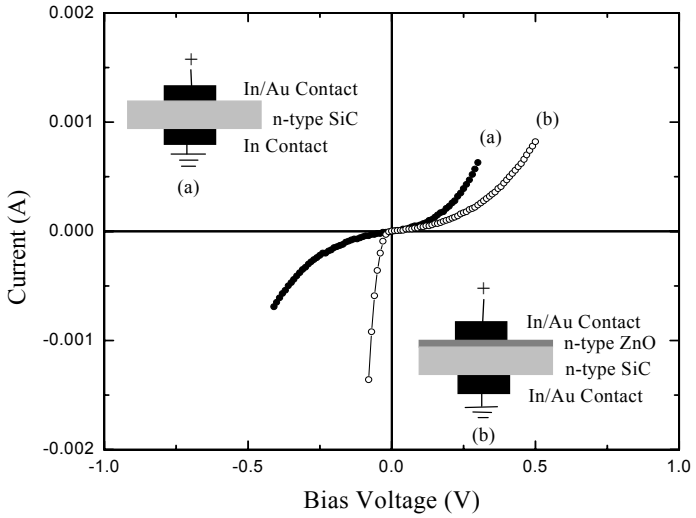


Figure 7. I–V characteristics of In/Au metal contacts on n-type SiC (curve (a)) and n-type ZnO/n-type SiC (curve (b)), that display a small potential barrier that results from a Schottky contact between In and n-type SiC, and a band offset between n-type SiC and n-type ZnO.

3rd STAGE ACCOMPLISHMENTS

The 3st Stage work demonstrated that we were able to fabricate and test ZnO diodes based on ZnO p-n junctions. The electrical properties (electroluminescence behavior) for ZnO diodes were measured. These achievements are summarized as follows:

ZnO Light Emitting Device Fabrication

For light emitting tests of ZnO p-n junction diodes, ZnO p-n layers were deposited on ZnO and SiC substrates, as described in the above two sections, 1st and 2nd Stage Accomplishments. The ZnO substrates are n-type (electron concentration ~ upper 10^{17} cm^{-3}), made by a high pressure melt growth technique (skull melting method), while the SiC substrates have a 3 x 10^{18} cm^{-3} electron concentration. The n-type substrates

were used to adapt the top-to-back contacts for current injection. The growth parameters for these ZnO layers are also explained above.

For electroluminescence measurements, ZnO layers were patterned (500x800 μm^2) for ZnO diode fabrication by using Buffered-Oxide-Echant (BOE) solution diluted with pure water (1:6 mixing ratio). The electrode contacts were made with Ni/Au (250x250 μm^2) metals that were deposited on the top face (ZnO:As surface) of the mesa, and In/Au metals deposited on the back side of the n-type substrate, as described above.

The I-V curves for one such set of ZnO diodes grown on n-type SiC and ZnO substrates are shown in Figs. 8 and 9. The ZnO p-n junctions on SiC show that the diode characteristics are improved by patterning the mesa structures for isolation, while ones on ZnO do not show such improvements. The ZnO p-n junctions on ZnO still show additional current leakage behavior as well as rectification properties of a p-n junction regardless of the mesa pattern. We do not clearly understand the reasons for such current leakages, although it seems to be caused by the ZnO substrate; for example, ZnO substrates, due to crystal quality and surface polishing skill, are not sufficiently good to produce high-quality epitaxial ZnO film growth. These (surface and/or bulk) current leakages for ZnO diodes on ZnO should be removed with surface passivation and further improvement of ZnO layer quality, which will be intensively studied in SBIR Phase II program efforts.

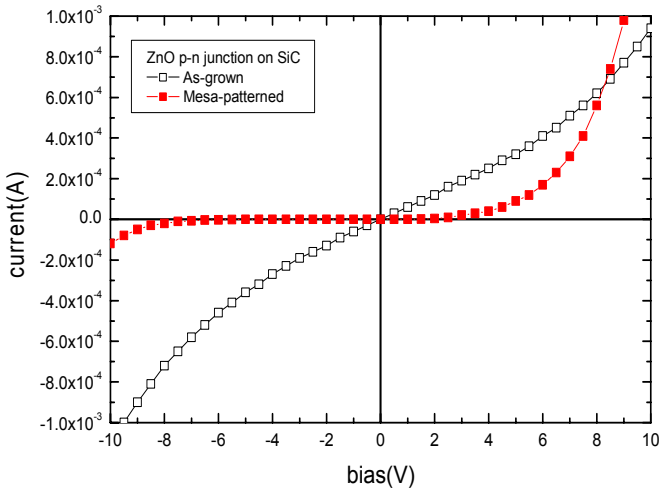


Figure 8. I–V characteristics of a ZnO p-n layer grown on SiC.

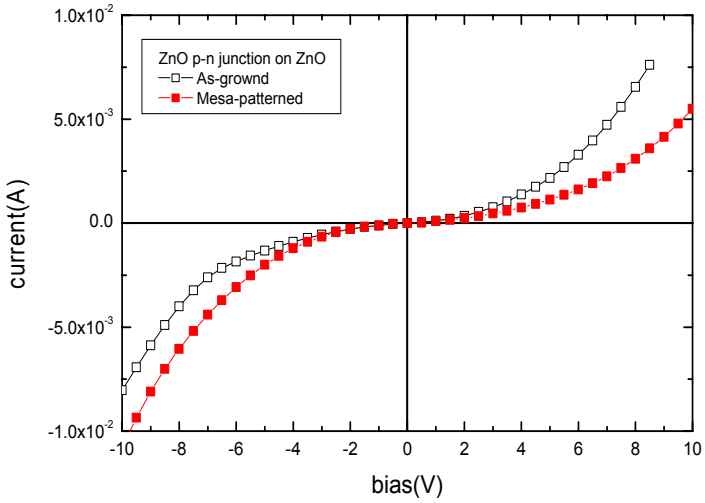


Figure 9. I–V characteristics of a ZnO p-n layer grown on ZnO.

Light Emission of ZnO Diodes

For electroluminescence studies of ZnO diodes in this SBIR Phase I effort, ZnO samples grown on n-type ZnO substrates were characterized. Although ZnO p-n layers

on SiC show better I-V characteristics as ZnO diodes than do those grown on ZnO substrates, we did not test ZnO diodes on SiC since those ZnO diodes may be affected (or damaged) by the process of removing a Schottky barrier that is formed between the metal (In/Au) contact to SiC.

Figure 10 is the photoluminescence (PL) spectra of a ZnO diode on ZnO measured at room temperature (RT). The dominant peaks are at 405 nm and 583 nm wavelengths. The first peaks are the band-edge emission lines and the second ones deep-level emissions due to defects. The fact that the 583 nm emission lines are significantly strong means that the ZnO substrates have huge number of defects. The crystal quality of the ZnO substrate should be improved for high-quality ZnO device fabrication.

ZnO diodes were operated at RT in a dc-pulse mode (peak width: 5 msec, and peak-to-peak interval: 0.5 sec) for EL characterization by current injection. Under low current injections (≤ 600 mA), these ZnO diodes reveal broad emissions located near 660 nm wavelength as shown in Fig. 11. Comparing with PL spectra, there is a 70-80 nm red-shift. Such a shift may be caused by either ohmic heating and/or Stark effects—a possibility that needs further study.

As the forward bias current was increased, the EL spectra were changed to several sharp emission peaks, as shown in Fig. 12, that were measured under a higher current injection (1 A). The change in shape of emission peaks as a function of the injected current indicates that the EL spectra in Fig. 11 and 12 were from different processes. The process for Fig. 11 is undoubtedly from spontaneous emission. It is possible that the process for Fig. 12 is stimulated emission; however, confirmation is necessary before making the assumption from these observations that RT lasing occurred in the ZnO p-n junction diodes. It should be noted that since we did not form a resonance cavity in the ZnO diode, these lasing processes may be occurring through Fabry-Pérot microcavities formed by the hexagonal ZnO microcrystallites. The latter supposition requires more intensive study.

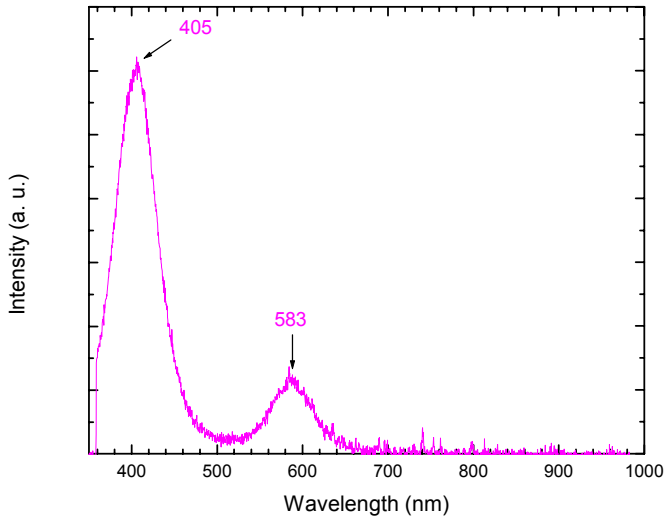


Figure 10. Photoluminescence spectra of a ZnO p-n junction diode measured at room temperature.

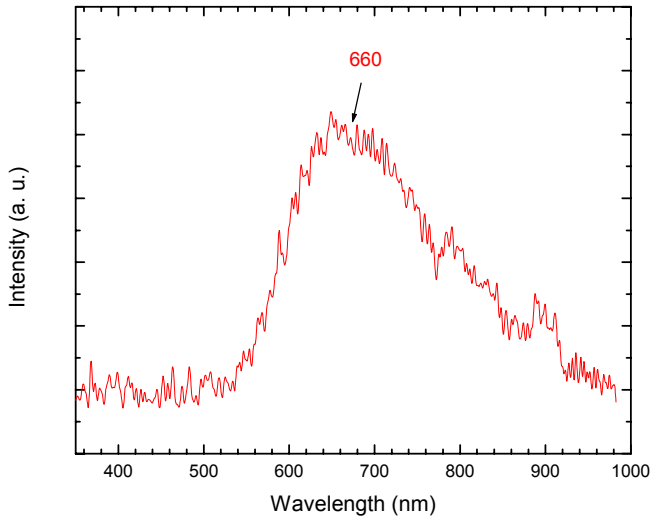


Figure 11. Electroluminescence spectra of a ZnO p-n junction diode measured at room temperature. The ZnO diode emits light by spontaneous emission.

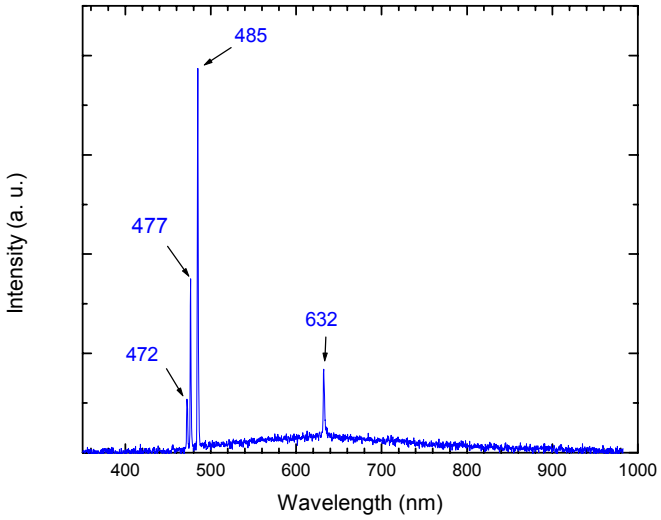


Figure 12. Electroluminescence spectra of a ZnO p-n junction diode measured at room temperature. Sharp peaks indicate that the ZnO diode emits light by stimulated emission.

Based on our successful results as summarized above, we conclude that ZnO-based light emitting devices can be fabricated in the near future.

V. PROPOSED EFFORTS FOR SBIR PHASE II PROGRAM:

The primary goal for a SBIR Phase II program is development of UV to visible light emitting diodes based on ZnO and its alloys. While devices that emit at several UV to visible wavelengths will be fabricated, we define our "target device" as one that will emit at 300 nm with power greater than 5 mW.

Although we have succeeded in demonstrating RT light emission, and possibly lasing, with ZnO diodes, several technical aspects should be improved for better operation. For example, i.) contact resistance should be drastically decreased for continuous mode operation, and ii.) current leakage should be eliminated.

To develop the target device it will be necessary to i.) engineer the bandgap of ZnO to a higher value (≈ 4.2 eV), ii.) design and fabricate quantum-well structures composed of ZnO and its alloy superlattices to improve the quantum efficiency of ZnO diodes, and iii.) package the device.

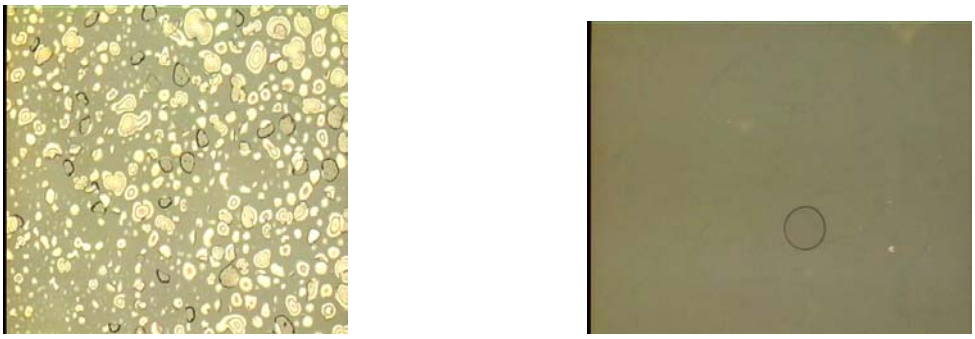
In SBIR Phase II efforts we will perform the following studies:

- Improve metal contacts to allow continuous operation of the diode devices at high power
- Improve the surface quality of the ZnO p-n junction to better understand the nature of the leakage mechanisms and to eliminate such currrents
- Increase the bandgap of the ZnO based material to ≈ 4.2 eV for an active layer to achieve 300 nm emission as well as for confining layers
- Design and fabricate quantum-well structures composed of ZnO and its alloy superlattices in the diode devices to improve the quantum efficiency and obtain light output power of 5 mW or greater, and
- Design and fabricate a packaged device that will have the necessary requirements for thermal stability and extended device lifetime.

Studies to address the needs associated with ohmic metal contacts, current leakage, bandgap engineering, quantum-well structures, and device packaging are described below.

Electrical Contacts and Current Leakage

The work initiated in the SBIR Phase I program will be continued to improve metal contacts and to reduce leakage current. We will explore two methods to reduce leakage currents: i.) use of higher quality ZnO substrates with improved surface preparation for epitaxial growth, and ii.) after-growth passivation of ZnO layers using a material such as silicon oxide. For example, figure 13 indicates that how the substrate affects the ZnO device characteristics and reliability.



(a) (b)

Figure 13. Microscopic images of silicon oxide layers deposited on ZnO layers. Image (a) is taken from a sample for which the ZnO layer was grown on a ZnO substrate (skull melting method). Image (b) is an image for which the ZnO layer was grown on a SiC substrate. The sample grown on the ZnO substrate shows a high-density of defects; whereas, the sample grown on the SiC substrate shows few defects.

Bandgap Engineering

For deep UV light emission at wavelengths near 250 nm, the bandgap (3.3 eV) of ZnO should be modulated toward a larger bandgap (≈ 4.2 eV). Elsewhere, an alloy of $Zn_{1-x}Mg_xO$ has been proposed for modulating the ZnO bandgap to higher energies. As the content of Mg is increased up to x = 0.33, the energy bandgap would be increased to 3.99 eV [A. Ohtomo et al.Appl. Phys. Lett. 72, 2466 (1998)]. However, a crystal phase separation occurs between MgO and ZnO if the Mg-content exceeds 0.33, due to the different crystal structure and large difference in lattice constants. MgO is cubic with 4.22 Å, and ZnO is hexagonal with 3.25 Å.

Instead, we propose an alloy of $Zn_{1-x}Be_xO$ be used rather than $Zn_{1-x}Mg_xO$ to achieve larger bandgaps. BeO (2.70 Å) and ZnO have hexagonal crystal structures with bandgaps of 10.6 eV and 3.3 eV, respectively [Yu. M. Aleksandrov et al. Sov. Tech. Phys. Lett. 7, 147 (1981); O. Madelung, Data in Science and Technology, Semiconductors other than Group IV Elements and III-V compounds, Springer-Verlag (1992)]. The energy bandgap for $Zn_{1-x}Be_xO$ can be expanded from 3.3 to 10.6 eV by

increasing Be concentration. For example, from a consideration of Vernard's Law, ZnO can be mixed with BeO in a proper ratio to attain a particular band gap value; more specifically, the energy band gap of $Zn_{0.9}Be_{0.1}O$ is greater by 0.73 eV than that (3.3 eV) of ZnO. This relationship is made clear in Fig. 14 that shows bandgap versus lattice constant values for ZnO, BeO and MgO. A small amount of Mg will be added to a $Zn_{1-x}Be_xO$ material to relieve stress caused by the lattice mismatch between ZnO and BeO.

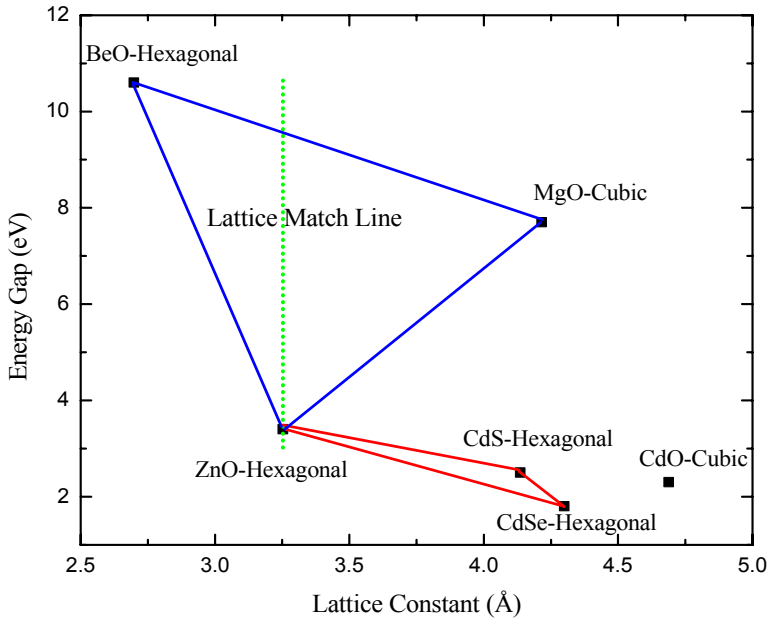


Figure 14. Bandgap versus lattice constant values for several materials.

Quantum-Well Structures

Quantum-well structures for ZnO based materials and devices will be designed and fabricated using the same approach as presented in the above section on bandgap engineering. The proportion of Be to Zn will be adjusted to obtain appropriate barrier heights and thickness to achieve the proper emission wavelength and high device efficiency.

Device Packaging

Devices will be packaged by a commercial foundry in standard TO cans. Devices will be characterized for light ouput, optical efficiency, thermal stability and longevity using industry standards.